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THE USE OF BASALT ROCKS FROM KOITASHSKOE ORE DEPOSIT IN PRODUCTION OF BUILDING CERAMICS AND FILTER MATERIALS

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The possibility of using recycled pyroxene scarn waste in the production of building ceramics is demonstrated.

Research in the field of production of new ceramic materials from abundant and inexpensive resources, including industrial wastes, is of great importance.

Basalt rocks, as well as the waste resulting from processed pyroxene scarns, are non-traditional materials which ultimately began to gain acceptance in the production of glass ceramics and stone-cast materials, and facing tiles, filter elements, and decorative coatings. Huge resources of such waste materials are accumulated near the Koitashskoe ore deposit. This waste product resulted from concentration of tungsten ore; it is fine-grained and has a dark green color with rare inclusions of light-colored minerals.

The main minerals comprising this waste are pyroxene (30 – 40%, here and elsewhere wt.% is indicated), quartz (30%), garnet (15%), calcite (5%) and sulfides (5%).

The granulometric composition of the waste product is as follows: 1.0 mm fraction — less than 1%; 0.5 – 1.0 mm — 1 – 2%; 0.1 – 0.5 mm — 40 – 50%; 0.043 – 0.1 mm — 17 – 24%; below 0.043 mm — 35 – 36%. The chemical composition is as follows (%): 41.0 – 48.0 SiO_2; 0.1 TiO_2; 3.7 – 5.0 Al_2O_3; 10.0 – 15.0 $FeO + Fe_2O_3$; 0.8 – 1.2 MgO; 20.0 – 24.0 CaO; 1.4 – 2.3 $K_2O + Na_2O$; 2.0 – 3.2 CO_2; 0.3 – 1.0 SO_3; 7.0 – 15.0 calcination loss.

The thermographic analysis performed on a Q-1500D unit revealed the relative heat inertness of the considered product. A few weak endothermic effects were observed, whose presence is probably related to structural changes in the impurity minerals. The fusibility of the material is characterized by a softening point of 1100°C and melting point of 1200°C.

The pyroxene product in combination with dolomite was used instead of the alkali-bearing component in the preparation of ceramic mixtures for interior decorative tiles.

The composition of the experimental mixtures was as follows (%): 55 – 65 Angrenskii clay, 30 – 40 pyroxene product, 5 dolomite.

The ceramic mixtures and the molding powder were prepared using a standard technology. Tiles 150 × 150 × 4 mm in size were compressed at a pressure of 20 MPa on two-stage bent-lever presses with hydraulic pressure control. Drying was carried out at the temperature of 150°C for 15 min. Single-stage firing was performed in the gas roll furnace at the Tashkent Building Materials Works with the accelerated procedure (55 min) and maximum temperature of 1140 – 1150°C.

The fired tiles exhibited water absorption of 16% and shrinkage of 2%. The moist expansion of the unglazed tiles was about 0.06%. The TCLE within the temperature interval of 20 – 600°C remained within the range of $(7.0 - 7.2) \times 10^{-6}\,°C^{-1}$.

The tiles were glazed by casting using boron-zirconium glaze. The glaze consumption for a 150 × 150 mm tile was 18 – 20 g (wet mass). The glaze was deposited on dried tiles which after firing had a good exterior appearance and satisfied the GOST 6141–91 requirements.

The tiles in service showed high crackle resistance, which is related to an increased content of alkaline-earth oxides (CaO). The bending strength of the glazed tiles based on pyroxene-bearing material was 60 MPa.

The possibility of producing decorative coating for ceramics based on recycled pyroxene scarns was studied. As can be seen from the chemical composition of the waste, it contains substantial amounts of Fe_2O_3 and FeO. However, it is known that the pigmentation of the material due to iron oxides is very sensitive in heating to the composition of the gas medium. Therefore, in order to obtain stable brown and black pigment, small quantities of copper, cobalt, chromium, and boron oxides were introduced in the waste composition. The additives were added to the crushed waste material, which was carefully mixed and calcined in an electric furnace at the temperature of 1000°C. The DTA curve of the coating exhibited one endothermic effect at the temperature of 173°C related to decomposition of H_3BO_3 in heating. No other heat effects were observed.

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The synthesized coatings were mixed with an additive of 6% bentonite and subjected to wet grinding to a residue of no more than 2% on a No. 0063 sieve. The obtained slip whose moisture content was 40% was deposited on ceramic tiles dried at 150°C which were made of the mixture containing pyroxene waste. The coating was deposited by spraying, by brush, or by immersion. Firing of the tiles at the temperature of 1150°C was performed in a laboratory electric furnace and in an industrial gas roll furnace. The waste-based coatings had stable black pigmentation in firing, regardless of the type of heating medium. The TCLE of the coating within the temperature interval of 20 – 600°C was equal to 6.8×10^{-6} °C^{-1}.

In developing the filtering elements which contain pyroxene waste as a filler, special investigations were carried out to select the binding materials for the mixture, since the binders ensure the required strength parameters of the raw material after molding and drying and the physicotechnical properties of the finished product after firing. The binders in porous ceramics should meet the following requirements:

– with a minimum content of binder, it should impart to the mixture a degree of plasticity sufficient for molding of articles;

– the binder should uniformly surround the filler particles and agglutinate them, imparting the required mechanical strength to the raw material.

Although the pore diameter and porosity are usually determined in the stage of mixture preparation and molding, the final shaping of the permeable structure of a porous ceramic material occurs in firing.

As was demonstrated in numerous investigations [1, 2], by decreasing the melting point of the binder it is possible to obtain a more uniform and efficient distribution of the binder over the filler surface, to improve the service parameters of the filtering elements.

Bentonite from the Azkamarskii deposit which is distinguished by sufficiently high plasticity and dispersion was selected as the main binder. The glass based on pyroxene waste with a melting point of 900 – 950°C served as an additive to this material. The investigation established that the binder content in the molding mixture should not exceed 25 – 27%. As was found in the experiments, in this case the binding mixture is uniformly distributed over the surface of the filler grains and develops a highly permeable porous structure.

The experimental prototypes of filtering elements shaped like plates were molded at the pressure of 3.0 – 5.0 MPa. Firing was done in electric furnaces at the temperature of 1100°C. The dispersion of the filler particles was 100 – 130 μm. The obtained products had the following properties: the average pore diameter was 66 mm, the maximum pore diameter was 75 μm, the open porosity was 35 – 37%, the air permeability was 75 – 90 μm^2, the bending strength was 8 – 10 MPa.

Thus, pyroxene scarn wastes from the Koitashskii ore field should be regarded as a promising and inexpensive material for production of building ceramics and filtering materials which operate in an aggressive environment.

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